

A Series of Aliphatic Dimethyl Amides

A Group of Isomeric Esters

A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
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JOHN R. RUHOFF

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A Series of Aliphatic Dimethyl Amides

Dimethyl amides have been prepared by several investigators,³ but the data on them are incomplete and not correlated. It seemed desirable to make a complete series of them so that comparisons can be made, not only between individual compounds, but also between this and other series. The eight dimethyl amides of the normal acids from formic to caprylic have been prepared and characterized. An unexpected discovery was that the acids except formic and their dimethyl amides give azeotropes boiling 4–5° above the amides. The data are in Table I and II. All of these dimethyl amides are mobile liquids which mix in all proportions with carbon disulfide, chloroform, carbon tetrachloride, benzene, ether, acetone and alcohol. The first two have limited solubility in petroleum ether, while the others mix with it. The lower members mix with water, but the higher homologs become increasingly insoluble; the solubility of VIII in water is less than 1%. In these respects dimethyl amides resemble esters, except that they are much more soluble in water and boil at substantially higher temperatures than esters of the same carbon content.

Another object was to investigate further the method of preparation of dimethyl amides recently proposed by Mitchell and Reid.⁴ Repetition of their work showed that dimethyl amides are formed in liberal amounts by their procedure, but that the reactions are not complete, except

with formic acid. Fractionation, taking very close cuts, gave what appeared to be pure compounds, but these proved to be azeotropic mixtures of the dimethyl amides and the acids. These azeotropes caused Mitchell and Reid to overestimate their yields and troubled van der Zande.⁵ The data on these constant boiling mixtures are brought together in Table II.

Experimental

Two equivalents of gaseous dimethylamine was passed into an acid which was heated under a reflux condenser from the top of which the excess of amine passed to a water trap. The water in the condenser jacket was kept warm enough to permit water vapor to escape. When there seemed to be no further reaction, the product was fractionated through a six-foot (2 meter) precision still,⁶ a narrow cut being taken at what appeared to be the boiling point. The products were found to contain free acid which was titrated with the results given in Table II. Several experiments were made with acetic acid, noting the temperature of the boiling mixture, and titrating samples of it after successive portions of amine had been added. No matter how much amine was passed in the liquid in the flask never became neutral.

Dimethyl acetamide was obtained in 78% yield by heating 360 g. of acetic acid, saturated with gaseous dimethylamine at 35°, for five hours at 200° in a steel bomb. Solid caustic potash was added to the product to take up water and acetic acid. The liquid thus purified was distilled at 162–165°; it was then dried and fractionated taking the cut 164.8–164.9° at 759 mm. Analysis showed this to be 99.25% pure. The dimethyl amides of butyric, heptioic and caprylic acids were made similarly. With the higher acids a new difficulty was encountered; the potassium salt of the acid is soluble in the dimethyl amide. In such cases the reaction product was taken up in a large volume of benzene and this solution shaken with potassium hydroxide solution, dried and distilled. Franchimont and Klobbie prepared heptioic dimethyl amide by this method.

Other dimethyl amides were obtained in good yields by adding the acid chloride dropwise during three hours to a

(3) (a) A. P. N. Franchimont, *Rec. trav. chim.*, **2**, 332 (1883); (b) A. P. N. Franchimont and E. A. Klobbie, *ibid.*, **6**, 247 (1887); (c) A. P. N. Franchimont and H. A. Rouffaer, *ibid.*, **13**, 336 (1894); (d) A. Verley, *Bull. soc. chim.*, [3] **9**, 690 (1893); (f) *J. Russ. Phys.-Chem. Soc.*, **29**, 227 (1897); (e) M. Tiffeneau and K. Fuhrer, *Bull. soc. chim.*, [4] **15**, 169–170 (1914).
(4) Mitchell and Reid, *J. Am. Chem. Soc.*, **53**, 1879 (1931).

(5) Van der Zande, *Rec. trav. chim.*, **8**, 233 (1889).

(6) Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

TABLE I

PHYSICAL PROPERTIES OF THE DIMETHYL AMIDES

Amide	M. p., ^a °C.	B. p., °C.	Press., mm.	d_4^{20}	d_4^{25}	n_D^{25}	M_D , obsd.	At. ref. ^b of N
I ^c	-61	153.0	760	0.9683	0.9445	1.4269	19.84	2.60
II ^d	-20	165.0	758	.9599	.9366	1.4351	24.24	2.49
III	-45	175.5	765	.9429	.9203	1.4371	28.75	2.40
IV ^e	-40	124.5	100	.9279	.9064	1.4391	33.39	2.43
V	-51	141.0	100	.9178	.8962	1.4419	38.08	2.52
VI	-42	158.0	100	.9099	.8896	1.4430	42.62	2.46
VII ^f	-19	172.5	100	.9051	.8854	1.4450	47.19	2.43
VIII	-21	187.0	100	.9002	.8810	1.4471	51.87	2.50

Average 2.49

^a The freezing points were determined with a copper-constantan thermocouple and potentiometer. ^b Obtained by subtracting the sum of the atomic refractions of all the atoms except nitrogen (Getman and Daniels, "Outlines of Theoretical Chemistry," p. 93) from the observed M_D . ^c Verley (ref. 3d) gives b. p. 155° and d^{20} 0.968; Franchimont and Rouffaer (ref. 3c) give b. p. 153° and sp. gr. 0.9525 at 15°; Bruhl [*Ph. Ch.*, **22**, 375 (1897)] gives b. p. 76° at 39 mm., $d^{22.4}$ 0.9484, and $n_D^{22.4}$ 1.42938. By interpolation our densities are 0.9493²⁰, 0.9540¹⁵, and 0.9469^{22.4}. ^d Franchimont (ref. 3a) gives b. p. 165.5° at 754 mm. and d^{20} 0.9405; Bruhl (*Ph. Ch.*, **22**, 376 (1897)) gives b. p. 83-84° at 32 mm., d^{20} 0.9434, and $n_D^{22.5}$ 1.43708. Our (calcd.) value is d^{20} 0.9413. ^e Tiffeneau and Fuhrer (ref. 3e) give b. p. 186-196°. Franchimont and Klobbie (ref. 3b) give b. p. 242.5-243.5° at 758 mm., and sp. gr. 0.894¹⁵, our d^{15} 0.893.

TABLE II

AZEOTROPIC MIXTURES OF ACIDS AND THEIR DIMETHYL

Amide	Boiling range, °C.	AMIDES			
		Pressure, mm.	Amide, %	Acid, %	Sum
I	153.2	757	97.4	1.2	98.6
II	170.8-170.9	761	77.2	21.1	98.3
III	179.2-179.4	767	75.8	23.4	99.2
IV	129.9-130.0	100	66.1	32.0	98.1
V	145.7-145.9	100	68.0	30.8	98.8
VIII	189.9-190.0	100	71.9	26.0	97.9

concentrated aqueous solution of three moles of the amine kept at -20 to -10°. The resulting mixture was satu-

TABLE III

ANALYTICAL DATA

Amide	Carbon, %		Hydrogen, %	
	Calcd.	Found	Calcd.	Found
III	59.35	59.40	10.97	11.35
V	65.05	65.67	11.71	11.65
VI	67.07	67.61	11.97	11.76
VIII	70.10	69.73	12.37	12.26

rated with potassium hydroxide in the cold, and the dimethyl amide separated and distilled.

The analyses of the new dimethyl amides, propionic, *n*-valeric, caproic and caprylic are given in Table III.

A Group of Isomeric Esters

The preparation and investigation of the group of esters having the formula RCOOR' , where R and R' are normal saturated aliphatic residues, containing fifteen carbon atoms together, were undertaken in connection with other work on the general problem of the relation of structure to physical properties. The present paper describes the synthesis and the determination of the more common physical constants of these compounds. Further physical and chemical studies are being carried on in this Laboratory.

Although certain of these esters have been prepared before, it was felt desirable, in order to make significant comparisons of physical properties, to have samples of comparable purity. All of the fifteen isomers have been made in quantities sufficient (usually 1 mole, 256 g.) to permit of a

TABLE I
PROPERTIES OF THE ISOMERIC ESTERS

C atoms in Alkyl group	Acid	B. p., °C. at 30 mm.	M. p., °C.	n_D^{20}	d_4^0	d_4^{26}	Coeff. of exp. $\times 10^4$	M _D ²⁰ (calcd. 77.62)
1	15	199.0	15.46 ^h	1.4390	Solid ^l	0.8618	8.91	77.86
2	14	195.0 ^a	11.94 ⁱ	1.4362	Solid ^m	.8573	8.96	77.83
3	13	194.0	— 5.74	1.4357	0.8748	.8555	8.90	77.92
4	12	194.0 ^b	— 6.84	1.4354	.8747	.8555	8.91	77.88
5	11	193.0	—21.17	1.4356	.8752	.8560	8.86	77.86
6	10	193.0	—17.67	1.4351	.8743	.8553	8.79	77.85
7	9	192.5 ^d	—15.54	1.4350	.8745	.8553	8.87	77.84
8	8	192.5 ^e	—18.08 ^f	1.4352	.8745	.8554 ^g	8.87	77.85
9	7	193.0	—11.14	1.4352	.8745	.8552	8.91	77.87
10	6	193.0	—19.29	1.4353	.8743	.8552	8.82	77.88
11	5	193.5	—23.14	1.4358	.8752	.8560	8.87	77.89
12	4	194.5 ^c	—22.64	1.4353	.8754	.8562	8.91	77.80
13	3	195.0	— 0.42	1.4363	.8767	.8574	8.94	77.84
14	2	197.0 ^k	14.00 ^j	1.4373	Solid ⁿ	.8581	8.97	77.93
15	1	201.5	13.69	1.4399	Solid ^o	.8618	8.93	78.00

^a B. p. atm. 295°, Reimer and Will, *Ber.*, **18**, 2016 (1885). ^b B. p. 18 mm. 180°, König and Otten, *Ann.*, **473**, 249 (1929). ^c B. p. 19 mm. 177–178°, König and Otten, *ibid.* ^d B. p. 75 mm. 210°, König and Otten, *ibid.* ^e B. p. atm. 305.9°, Gartenmeister, *Ann.*, **233**, 289 (1886). ^f M. p. —9 to —12°, Gartenmeister, *ibid.* ^g d_4^{26} 0.8755, Gartenmeister, *ibid.* ^h M. p. 10°, Eckert and Halla, *Monatsh.*, **34**, 1821 (1913). M. p. 18.5°, Le Sueur, *J. Chem. Soc.*, **87**, 1898 (1905). ⁱ M. p. 10.5–11.5°, Nördlinger, *Ber.*, **18**, 2623 (1885). M. p. 11.93°, Meyer and Reid, Ref. 4. ^j M. p. 14.01°, Meyer and Reid, *ibid.* M. p. 11°, Garner and Rushbrooke, *J. Chem. Soc.*, 1351 (1927). M. p. 12–13°, Krafft, *Ber.*, **16**, 1720 (1883). ^k B. p. 15 mm. 175.5–176.5°, Krafft, *ibid.* ^l d_4^{35} 0.8541. ^m d_4^{35} 0.8497. ⁿ d_4^{35} 0.8503. ^o d_4^{35} 0.8541.

high degree of purification and to allow the determination of a wide range of physical and chemical properties.

Emphasis was placed primarily on the preparation of compounds of the highest purity consistent with the attendant experimental difficulties, rather than on high yields. Yields are therefore not reported, but in almost all reactions they were 70% or more. All distillations were carried out in precision stills.³ Each intermediate was fractionated; except in a few instances, the portion used for synthesis boiled with a range of 0.4° or less.

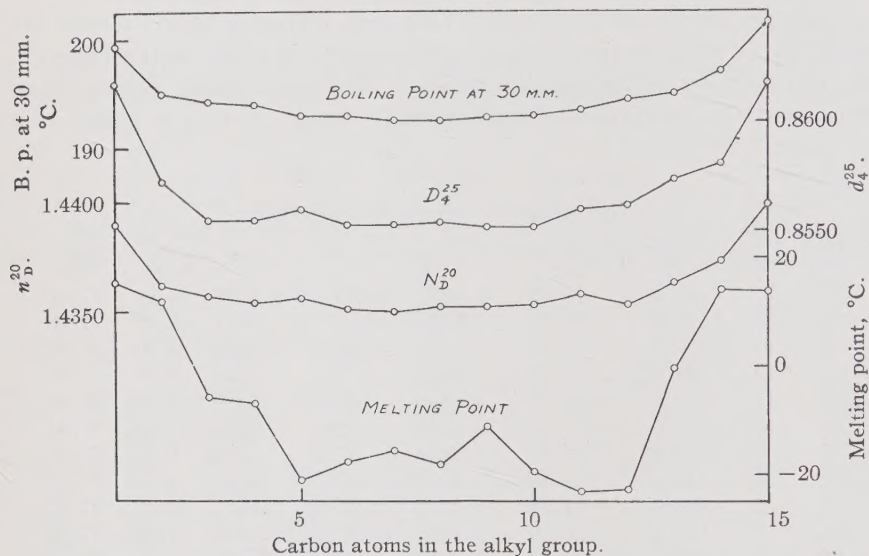


Fig. 1.

The results of the physical measurements are given in Table I and summarized in Fig. 1. When the data are plotted against the number of carbon atoms in the alcohol, the curves obtained for the boiling points, refractive indexes, and densities are very similar. Distinct alternation of the refractive indexes and densities occurs near the ends of the curves; the values for the middle five esters are practically identical. It is noteworthy that high values are found for the 5-11 and 11-5 compounds. The boiling points are remarkably close together; the extreme range is 9° and all except three of the compounds boil within 2.5° of each other. The melting points, on the other hand, cover a range of almost 40°; for the most part they show alternation.

Experimental

(A) Alcohols.—Amyl alcohol was prepared by the Grignard reaction from butyl bromide and formaldehyde. Hexyl, nonyl, undecyl, tridecyl, tetradecyl, and penta-

(3) Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

decyl alcohols were prepared by the reduction of an ester of the corresponding acid with sodium in butyl alcohol.⁴ Octyl, decyl and dodecyl alcohols were obtained by the fractionation of "Lorol," purchased from Germany. Heptyl alcohol was prepared by the reduction of heptaldehyde with iron filings in acetic acid,⁵ with a small amount of nickel chloride as a catalyst. Baker 40-mesh degreased cast iron fillings were used. In over fifty reductions made in this Laboratory, the reaction has never failed to occur when nickel chloride was added.

(B) Acids.—Valeric, tridecylic and pentadecylic acids were prepared from the proper bromides and potassium cyanide.⁶ Caproic and pelargonic acids were prepared by the malonic ester synthesis from butyl and heptyl bromides, respectively. Anhydrous butyl alcohol was used as a solvent. Caprylic, capric, lauric and myristic acids were obtained by the fractionation of the ethyl esters made from coconut oil acids. Undecylic acid was obtained by the hydrogenation of ethyl undecylenate at 220°, using a high speed stirrer⁷ and 4% of nickel formate as a catalyst. Heptoic acid was prepared by the oxidation of heptaldehyde with potassium permanganate and 20% sulfuric acid at 20°.

(C) Esters.—Methyl pentadecylate, ethyl myristate and propyl tridecylate were prepared by heating together 1 mol of the acid, 4 mols of alcohol containing 3–5% of anhydrous hydrochloric acid, and 30 g. of anhydrous calcium chloride.

Butyl Laurate.—To 1 mol of lauric acid was added 3 mols of anhydrous butyl alcohol, containing 20 g. of anhydrous hydrochloric acid. After the solution had been refluxed a short time two layers formed. The lower (water) layer was removed, and the butyl alcohol distilled off slowly.

Amyl Undecylate, Hexyl Caprate, Heptyl Pelargonate, Octyl Caprylate, Nonyl Heptoate, Decyl Caproate and Undecyl Valerate.—One mol of alcohol, 1 mol plus 10 g. of acid, and 15 g. of anhydrous hydrochloric acid were warmed together until two layers were formed. The lower layer was removed, and the residue was gradually heated to 180° during the course of two hours while a slow stream of carbon dioxide was passed through it.

Dodecyl Butyrate and Tridecyl Propionate.—One mol of alcohol, 1.5 mols of acid (3 mols in the case of the propionic acid), and 25 g. of anhydrous hydrochloric acid were distilled together slowly until the boiling point rose to that of the acid.

Tetradecyl acetate was prepared from the alcohol, acetic anhydride and sodium acetate by the usual well-known procedure.

Pentadecyl Formate.—One hundred and eighty grams of pentadecyl alcohol, 460 g. of 90% formic acid and 400 cc. of carbon tetrachloride were heated in a continuous esterification apparatus for twenty-four hours; at the end of that time the reaction was 85% complete. The pentadecyl formate and the residual pentadecyl alcohol were separated and refluxed for six hours with 460 g. of anhydrous formic acid.⁸ The ester layer was separated and distilled slowly with 600 cc. of carbon tetrachloride and 230 g. of anhydrous formic acid until the boiling point rose to 100°.

Purification of Esters.—The esters, with the exception of pentadecyl formate, were washed twice with warm water, then with warm 1 to 50 ammonia water, twice with warm water again, dried with calcium chloride, filtered, and distilled at 30 mm.

Freezing Points.—The freezing points were determined with a copper-constantan thermocouple in an apparatus designed by R. H. Smith, and similar to that described by Andrews, Kohman and Johnston.⁹

(4) Meyer and Reid, *J. Am. Chem. Soc.*, **55**, 1574 (1933).

(5) Clarke and Dreger, "Organic Syntheses," Vol. VI, p. 52.

(6) Adams and Marvel, *J. Am. Chem. Soc.*, **42**, 312 (1920).

(7) Milligan and Reid, *Ind. Eng. Chem.*, **15**, 1048 (1923).

(8) Garner, Saxton and Parker, *Am. Chem. J.*, **46**, 236 (1911).

(9) Andrews, Kohman and Johnston, *J. Phys. Chem.*, **29**, 914 (1925).

TABLE II
ANALYTICAL DATA ON NEW COMPOUNDS

Compound	%C	%H	Saponification value	Compound	%C	%H	Saponification value
Calcd.	74.93	12.59	256.3	Calcd.	74.93	12.59	256.3
3-13	74.81	12.66	259.3	10-6	74.85	12.43	258.1
5-11	74.94	12.46	256.7	11-5	74.92	12.69	258.2
6-10	74.88	12.59	256.3	13-3	74.94	12.51	258.8
9-7	74.91	12.61	258.0	15-1	75.10	12.65	259.5

VITA

The author, John R. Ruhoff was born in De Pue, Illinois in 1908. He received his early education in the public schools of Madison, Wisconsin. He entered the University of Wisconsin in 1925, and was graduated with the degree of Bachelor of Science in 1929. He was a student in the department of chemistry in the graduate school of The Johns Hopkins University from October 1929 to June 1933. During his residence he held the Kewaunee Manufacturing State Fellowship for Wisconsin.

